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14. ABSTRACT
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ABSTRACT

Progress is reported on tuning the band-gap of cuptic oxide nanosheets and a host of applications.
New collaborations greatly strengthen this work particularly the addition of theoretical work of Batista in Chemistry at Yale. This will help to understand structure/band gap relationships.

Copper Oxide (CuO) 2-D Nanosheets for Advanced Electronic and Optical Properties

Lisa Pfefferle, Yale University, Department of Chemical and Environmental Engineering

ARO # 64935-MS Agreement W911NF-14-1-0564

Period covered by report 2/5/2015-7/31/2015

In the 10 months of this project we have:

1. A wide variation of band gap has been reported for CuO nanomaterials. We have characterized the band gap of a wide range of our CuO nanosheets after annealing in oxidizing and reducing conditions at different times and found consistent variations between 1.1 and 1.9eV. The differences are proposed to be due to both oxygen vacancies, mixed states and structural changes. Victor Batista (Yale Chemistry) is using first principles modeling to understand the mechanism. We believe that this will lead to the ability to easily tune the bandgap and may lead to new graded band gap devices.

2. A paper on the antibacterial activity of the cupric oxide nanosheets is in near-final form and a full draft is included with this report.

3. We are continuing work on arsenic and selenium adsorption and a paper is being drafted.

4. A new thrust to exfoliate and intercalate the CuO sheets using a supercritical CO_2 reactor is in progress. The reactor is being machined and experiments will begin September 1.

5. Transport measurements on pellets made of the sheets are beginning along with electrochemical measurements.

6. In-situ doping with Strontium has been accomplished. High salt concentrations lead to Sr-doped CuO nanotubes.

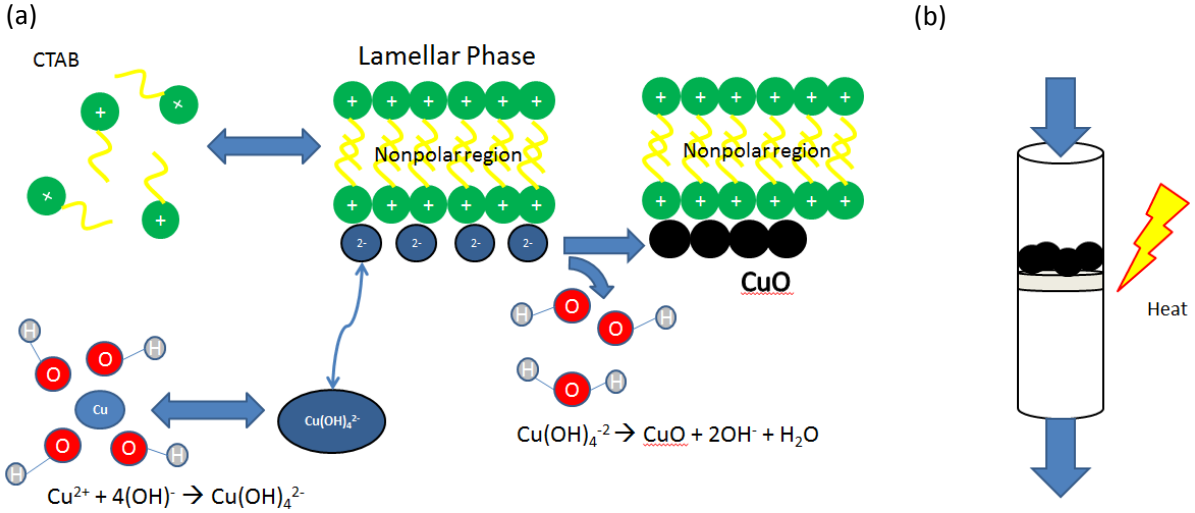
7. Results from Synergistic projects: We have gotten some good preliminary results on a sensor platform from Professor Nancy Savage at the University of New Haven. The research is also benefiting from calculations the group of Victor Batista (Yale Chemistry) using first principles modeling to understand how structure and defects affect the electronic properties of the material. Professor Julie Zimmerman's group has been testing the anti-microbial properties of the nanosheets and the attached paper demonstrates the results showing that they are more active than conventional CuO mamterials. In another collaboration with the Zimmerman group we are exploring the potential for the CuO nanosheets for the upgrading of biodiesel. In a collaboration with Professor Kim at Yale we have decorated CuO nanosheets with nanodiamonds as a new catalytic format.

Below we give details from selected of these projects and a draft of the antibacterial paper is included in separate files.

I. Tuning the Band Gap of Cupric Oxide Nanosheets

Several challenges continue to impede wide spread adoption of solar technology such as high material cost, material toxicity, and low efficiency.[1] The energy difference between a material's valence band and conduction band (i.e. the band gap) determines how efficiently it absorbs sun light. Cupric Oxide is a nonhazardous, highly abundant p-type semiconductor with a reported band gap ranging from 1.2 eV to 2.0 eV.[2,3,4] The reason for this wide range is unknown, though we propose they are due to structural and/or compositional defects (e.g. oxygen vacancies). We hypothesize that the properties of cupric oxide nanosheets, such as its band gap, may be tuned through mild oxidative or reductive treatments.

2D nanomaterials as opposed to their 0D or 1D counterparts are ideal for solar applications because their density of states is a step function with respect to energy rather than a sharp peak.[5] This allows 2D materials to absorb a greater fraction of broad spectrum light, such as that emitted from the sun. Additionally, owing to their high surface area, cupric oxide nanosheets show increased reactivity when compared to their bulk counterparts. This makes them an ideal candidate for band gap tuning through non-degradative synthesis techniques.



The schematic above depicts the mechanism by which CuO nanosheets are synthesized (a) and treated (b). In an aqueous solution, hexadecyltrimethylammonium bromide (CTAB), a positively charged surfactant, self assembles into a lamellar structure at high pH. The negatively charged copper hydroxide complex is electrostatically attracted to the surface of the CTAB scaffold and reacts to form cupric oxide in nanosheets. The nanosheets are then washed and the dry powder is heated in a reactor for different amounts of time.

Cupric oxide nanosheets were synthesized via an aqueous phase surfactant templating[6] process and then baked at 350°C in oxygen for 30, 60, and 120 minutes as drawn in schematic 1 above. UV-visible spectroscopy data was collected on samples for each treatment time and their band

gaps were determined by Tauc Plot analysis.[7] The results are shown below in figure 1. It was found that after 30 minutes of treatment the band gap of the CuO nanosheets increased from 1.26 ±0.02 eV to 1.79 ±0.01 eV. It then decreased to 1.56 ±0.02 eV after 60 minutes of treatment, and to 1.21 ±0.1 eV after 120 minutes. This trend may be the result of two (or more) competing processes. For example the oxidative treatment may cure oxygen defects sites and increase nanosheet crystallinity, though this may be counterbalanced by a loss of nanostructure from sintering. SEM images of CuO nanosheets are also presented in figure 1. After 30 minutes no degredation in structure is observable, but smoothing and rounding of the edges does become present after 60 minutes and noticeable after 120 minutes.

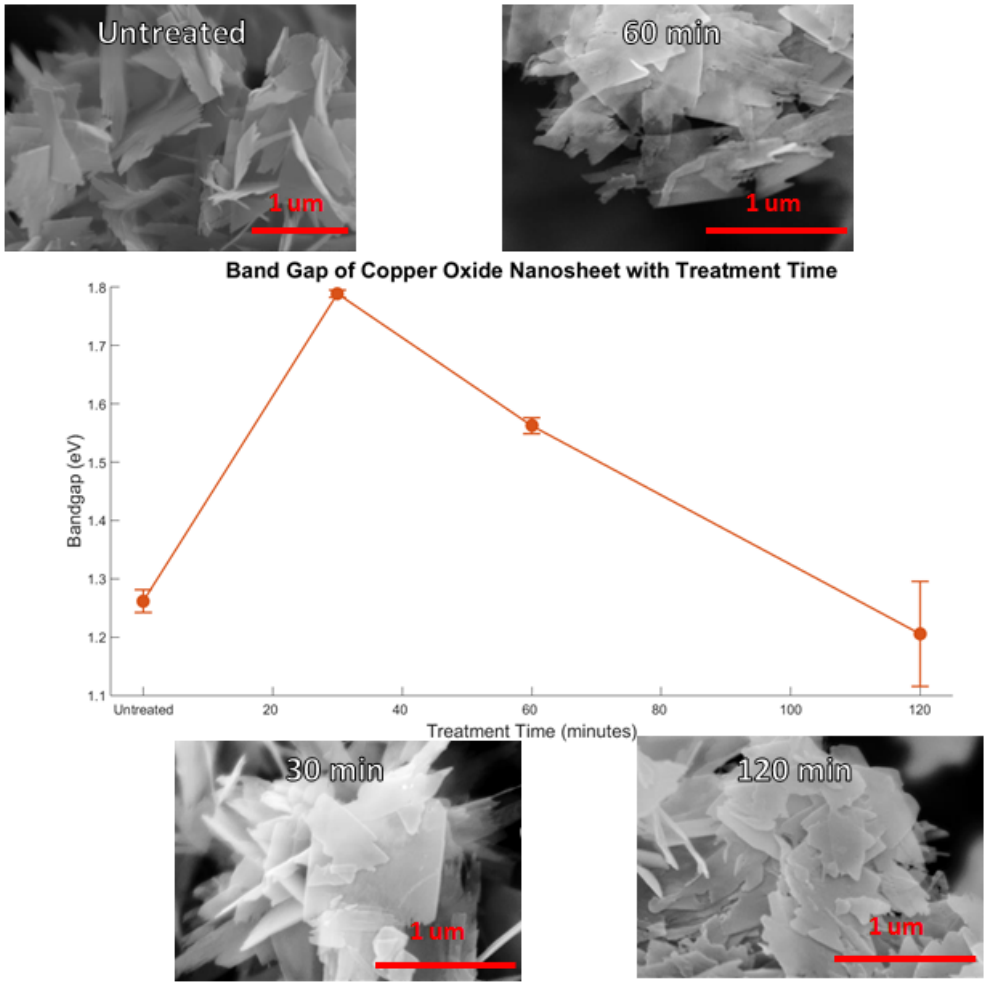


Figure 1 above shows the band of cupric oxide nanosheets after annealing for different times (30, 60, 120 min) in oxygen accompanied by SEM images of their structure. The band gaps were determined by UV-Visible spectroscopic data collected and subsequent Tauc plot analysis. Measurements were made in triplicate. Each point represents the mean band gap measured and the error bars signify one standard deviation from that mean.

Additionally temperature programmed oxidation of CuO nanosheets in 4% isotopic oxygen (O^{18}_2 atmosphere) was conducted (data not shown). At 350°C there was an increase in $O_2^{16,18}$ detected by the mass spectrometer, that is Oxygen gas containing one O^{18} and one O^{16} atom. Since the only source of O^{16} was from the cupric oxide nanosheets and the only source of O^{18} from the flow gas, this seems to suggest oxygen mobility and exchange is occurring similar to a Mars-Van Krevelen reaction.[8]

Further work both experimentally, such as the characterization of in-situ oxygen coordination through X-ray absorption fine edge spectroscopy (XAFS), and theoretically, using advanced computational models, is being addressed to determine the mechanism by which these structural perturbations result in property changes. Once this is understood, the properties of CuO nanosheets and other materials may be designed *a priori* and tuned for solar cells, photocatalysis, and other applications.

We are also exploring solution methods for milder reduction and oxidation to maintain the structure better during these processes.

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II. Exfoliation, Intercalation and Doping

To obtain superconductivity a number of approaches are being attempted to decrease the thickness of the CuO nanosheets as well as incorporate other atoms into their lattices. Exfoliation, a technique being used to create single layer graphene sheets from bulk graphite, will be applied to CuO nanosheets to sheer the sheets apart. We will be using supercritical CO_2 that has been shown to swell the sheets of graphene and then by quickly decompressing the mixture hopefully cause the CO_2 trapped between the sheets to blow them apart.

We hope to also use this SC-CO2 method to intercalate dopants in between the layers of the CuO nanosheet. By co-dissolving salts such as Lanthanum and Strontium Nitrate we believe that the CO_2 will create avenues for these dopants to infiltrate between the layers of the CuO nanosheets.

Another approach we are working on is introduction of these dopants during synthesis. Millimolar concentrations of Strontium Nitrate were dissolved in the CuO nanosheet synthesis solution and the product was observed. At high Strontium concentrations both CuO nanotubes and nanosheets were formed. Through SEM and EDX we have found that at high concentrations of Strontium in the CuO products formed. Low temperature conductivity measurements will be conducted in the coming months as well as Lanthanum doping.

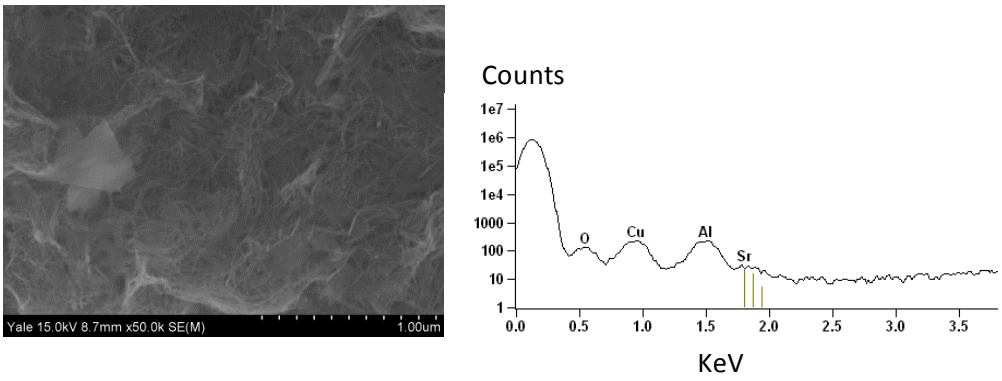


Figure 2 (left) shows SEM image of Strontium doped CuO nanotube and nanosheets accompanied by (right) EDX spectra positively identifying strontium.

III. Composite formation, Templating and Functionalization

Earlier in this project it was found that addition of Ferrous Sulfate to CuO nanosheet solution resulted in the formation iron oxide nanosheets as observed by TEM (fig 3). Hematite, a specific type of iron oxide, has been found to be an effective photocatalyst in water splitting reactions. By FTIR analysis it appeared that these sheets are not a single phase of iron oxide, but are a collection of many different types of iron oxide. The challenge remains to convert these iron oxide sheets into hematite, which can then be used alone or in conjunction with copper oxide nanosheets for photocatalytic reactions such as water splitting and CO2 to methanol conversion. They may also be useful as templates themselves to resynthesize thinner copper oxide nanosheets.

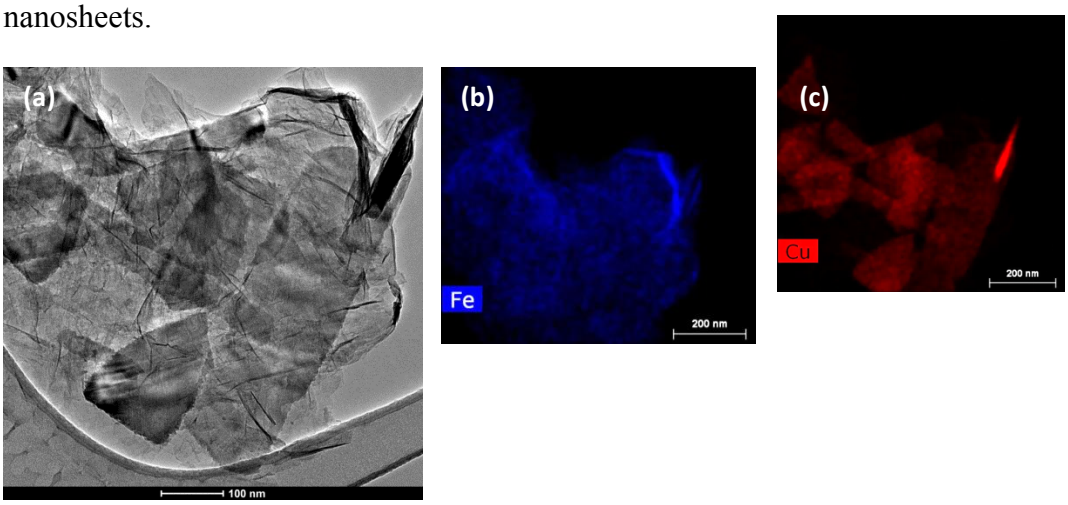
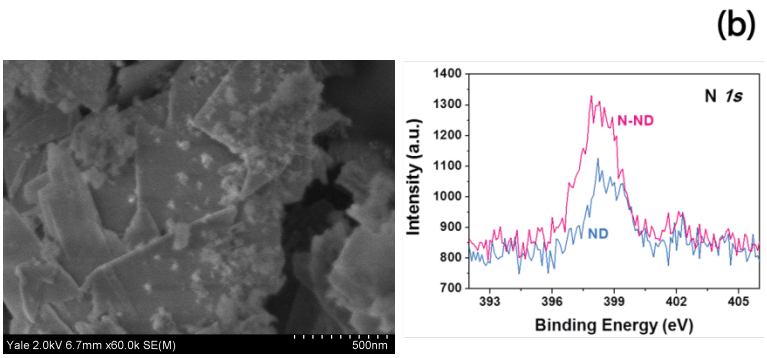
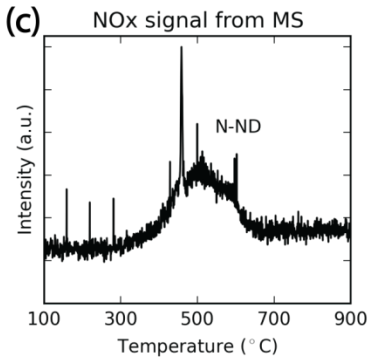


Figure 3- (a) TEM image of copper oxide and iron oxide nanosheets. EDX mapping shows the location of copper (b) and iron (c) in the sample. The copper oxide nanosheets seem to be more rigid while even wrinkles seem to be present in the iron oxide sheets.

Copper oxide nanosheets decorated with nitrogen doped nanodiamonds were synthesized (figure 4). Nanodiamonds in and of themselves are not useful for photocatalysis, however doped nanodiamonds joined with other materials have shown promise, replacing precious metal catalysts. When NDs are combined with photocatalysts, the sp2 conducting carbon layer on the surface of NDs can separate and transport electrons like a conduit. In order to maximize the photocatalytic activity of ND/photocatalyst composites, the electrical conductivity of NDs must be increased because defects or irregularities in the conducting surface carbon layer may expose their insulating diamond core.[4]





(d)

Atom Percentage		
Element	ND (%)	N-Doped ND (%)
Carbon	90.53	91.76
Nitrogen	1.47	3.19
Oxygen	8.00	5.06

Figure 4 depicts (a) an SEM image of nitrogen doped nanodiamonds on CuO nanosheets, (b) XPS data at the Nitrogen edge of doped (N-ND) and undoped (ND) nanodiamonds, (c) NOx signal (m/z 30) from mass spectroscopy of nitrogen doped nanodiamonds during temperature programmed oxidation (TPO), and (d) the calculated atom ratios of undoped and doped nanodiamonds as calculated from the XPS results (cooraborated TPO results).

Our collaborators at NASA found that they were able to grow graphene on CuO nanosheets by chemical vapor deposition. However heating to such extreme temperatures (approx. 1000C) in methane most likely destroyed the nanosheets, making them no different than any other copper catalyst. However it may be possible that this can be done at lower temperatures. For example CuO nanosheets refluxed in dichlorobenzene for 12 hours causes them to exhibit strong hydrophobic tendencies. This was observed through addition of water. Untreated CuO nanosheets preferred the aqueous phase while CuO nanosheets refluxed in dichlorobenzene preferred the organic phase. We posit that dichlorobenzene is chemically attaching to the surface of CuO nanosheets, displacing hydroxyl groups. We believe that annealing of these rings on the surface of CuO nanosheets may lead to low temperature graphene formation. Additionally these functionalized CuO nanosheets may have applications in membranes where hydrophobicity is necessary.

IV. Details of Synergistic projects

IV.1 CuO nanosheets for Biodiesel synthesis

Professors at Yale University are coming together to form an all in one center for the understanding of biodiesel, from its production in algae with Dr. Jordan Peccia's group, to its

extraction with Professor Julie Zimmerman's group, to its catalytic reforming and combustion as a fuel with Professor Lisa Pfefferle's group. Between the production and extraction step though is a conversion step from triglycerides to fatty acid methyl esters (FAMEs). Metal oxides on copper and copper Oxide supports have been investigated by some groups as efficient and selective catalysts for conversion of triglycerides to FAMEs, the most touted of these SrO.[1,2] We intend to investigate our synthesized Strontium doped CuO nanosheets as a catalyst for this conversion.

IV.2 CuO nanosheets as an enzyme mimetic and glucose sensor

In collaboration with Dr. Nancy Savage from the University of New Haven we are investigating the potential of CuO nanosheets as an enzyme mimetic for the sensing of glucose. Preliminary results show that CuO nanosheets are as good as what has been reported in the literature[3], but through surface functionalization (e.g. with hydroxyl groups) we believe it will be possible to increase this sensitivity.

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